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Synthetic Organic Chemicals

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The Determination of Metals with 8-Hydroxyquinoline

ONE of the new organic reagents rapidly growing in favor with analytical chemists is 8-hydroxyquinoline. The phenolic hydrogen of this compound is readily replaced by metals, forming, in many cases, insoluble colored precipitates. Through the difference in solubility of these precipitates many valuable separations can be made. The reactions of various metals with 8-hydroxyquinoline have been the subject of several investigators, both in this country and abroad. R. Berg, of Königsberg University, in particular, has made a careful study of the analytical applications, the results of which have appeared in *ZEITSCHRIFT FÜR ANALYTISCHE CHEMIE* during the past two or three years.

The most extensive use of this reagent at present is in the determination of aluminum, although methods are available for magnesium, zinc, cadmium, bismuth, manganese, iron, uranium, and titanium. The color of the precipitate in most cases is greenish-yellow, although the ferric complex is black and the ferrous compound red.

There are a number of methods which may be used to determine the amount of the insoluble precipitate. The simplest is to dry at 100°C . and weigh directly, since all of the precipitates have a definite composition. The calculations are sometimes complicated by the fact that

a few of the compounds form hydrates which are stable at 110°C . In these cases it is best to heat to 140°C . to remove the water of crystallization. The precipitate can also be ignited to the metallic oxide, in which case mixture with a little oxalic acid before ignition is recommended to prevent any loss through volatilization. The most satisfactory means of evaluating the precipitate is to break up the complex with dilute hydrochloric acid, regenerating the 8-hydroxyquinoline. The liberated hydroxyquinoline is then titrated with a potassium bromate-bromide solution.

The separation of the metals from one another is effected by varying the acidity of the solution in which precipitation takes place. Hydroxyquinoline itself is rather insoluble in water but can be dissolved in alcohol, acids, and alkalis. As a reagent it ordinarily is used in the form of a 2-4% solution in dilute acetic acid. When dissolved, however, the reagent is not as stable as the dry material. Its solution in inorganic solvents is characteristically yellow, so in precipitating a metal the reagent is added until the yellow color of the supernatant liquid shows that an excess is present.

Owing to the difficulty in the separation of aluminum by other methods, Lundell and Knowles, of the U. S. Bureau of Standards, have described a

procedure which gives an 8-hydroxyquinoline precipitate entirely free of phosphorus, arsenic, fluorine, or boron. The reagent in this case is a 2.5% solution of 8-hydroxyquinoline in dilute acetic acid. This is added in excess to the weakly acidified solution of the metal. The precipitate formed when ammonium hydroxide is added can more easily be filtered by warming for a time at 60-70° C. to increase the size of the crystals. Washing is carried out with a dilute solution of ammonium hydroxide containing a little of the reagent. The amount of aluminum can be determined by treating the precipitate with nitric and sulfuric acids to destroy the organic group, precipitating with ammonium hydroxide and finally igniting to aluminum oxide. The interference of vanadium, tantalum, titanium, or molybdenum, can be avoided by adding a few cubic centimeters of hydrogen peroxide to oxidize their salts to a higher form.

The similarity between beryllium and aluminum has sometimes made their separation difficult. However, if the hydroxyquinoline precipitation takes place in a solution just barely acid and containing ammonium acetate, the aluminum present will come out quantitatively while the beryllium will remain in solution. This insolubility of the aluminum compound in very weak acids also allows its separation from magnesium, since the magnesium precipitate is readily soluble under these conditions. In case the magnesium also is to be determined, it can easily be precipitated by making the filtrate ammoniacal. In alkaline tartrate solution, the solubilities of these two precipitates are reversed. Consequently, when small amounts of magnesium are to be separated from larger amounts of aluminum, it is more convenient to add the hydroxyquinoline to an alkaline tartrate solution of the metals, in which case it is the magnesium precipitate that comes out.

The hydroxyquinoline method for

magnesium is much more sensitive than the customary phosphate precipitation. It is used in the ceramic industry for determining magnesia in silicates, and in biochemical work for estimating magnesium in blood serum. A rapid colorimetric method for determining the magnesium content of boiler feed waters up to 50 parts per million, has recently been described. In this method, a standard solution of 8-hydroxyquinoline is used. After treating the standard with the magnesium sample, the decreased intensity of the yellow color is measured in a colorimeter. By subtraction this gives the amount of reagent used in the precipitation, from which the magnesium present can be calculated.

Zinc can be precipitated from solutions with 8-hydroxyquinoline although some other metals such as copper and cadmium also come down under the same conditions. The method is quite satisfactory, however, for magnesium-zinc alloys since in mildly acid solutions the magnesium remains in solution. Like magnesium, the zinc precipitate is insoluble in alkaline tartrate solutions, thus permitting its separation from aluminum, ferric iron, and chromium. Cobalt, nickel, lead, and bismuth cause some trouble which can be overcome by redissolving the zinc compound and precipitating again. All of these precipitates are easily and accurately evaluated by bromometric titration.

Copper and cadmium behave very much like zinc toward 8-hydroxyquinoline. Both are precipitated in alkaline tartrate or in solutions of acetic acid containing sodium acetate. In the acetic acid solution there is just enough difference in solubility of their hydroxyquinoline compounds so the two can be separated. The copper complex is still insoluble even in 10% acetic acid while at that concentration the cadmium compound remains entirely in solution.

The greenish-black iron precipitate is

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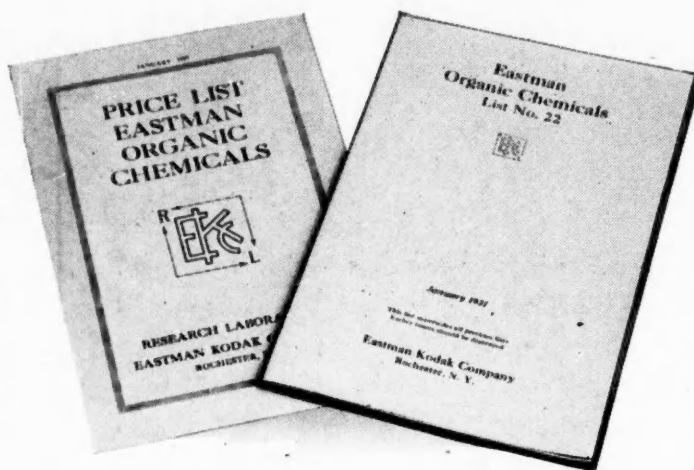
Eastman Organic Chemicals

THE twenty-second catalog of organic chemicals supplied by the Research Laboratories of the Eastman Kodak Company was issued in January. It contains over 2,700 items which are available to the various research laboratories throughout the country. The first list published in 1919 contained less than 150 items. Every year, the number of chemicals has increased and this new edition includes about 140 more items than the last.

The majority of the new chemicals are of interest principally to organic chemists engaged in synthetic work. Many of them, however, will be useful in other branches of chemistry as well. Possibly the most interesting addition during the year is *fluorobenzene*, which is the first organic compound with fluorine as a constituent to be included in the list. Fluorobenzene is a clear, colorless liquid (s.g. 1.024) boiling between 84° and 85° C. It completes the series of monohalogenated benzenes.

Physiological chemists will be interested in *α-methyl choline chloride* on account of the marked action of choline derivatives in reducing blood pressure. The study of the influence of the sulfhydryl group on cell growth will be aided through the addition of *o*- and *m*-thiocresol. Investigation of the toxic properties of organic phosphates in connection with the epidemic of "ginger" paralysis resulted in the listing of *tri-m-cresyl phosphate*.

While *phenylhydrazine* was one of the first chemicals to be included in the list, the reduction in the cost of the Eastman



The first list of Eastman Organic Chemicals (left) consisted of four pages—List No. 22 (right) contains one hundred.

grade to nearly one-third of last year's price almost entitles it to classification as a new chemical.

The increased use of organic chemicals in analytical work also brought about marked reductions. *Cupferron* and *8-hydroxyquinoline* are listed in the new catalog at just one-half their former price. New reagents prepared during the past year principally for use in analysis include *dichlorofluorescein*, an indicator for chloride titrations; *sodium diethyldithiocarbamate*, a sensitive reagent for copper; and *dime-thylpyrazole*, a cobalt precipitant.

Organic chemists now have available the *3,5-dinitrobenzoyl chloride* so useful in identifying alcohols and mercaptans. Adipic acid became available commercially during the year, as a consequence of which a number of the esters and other derivatives have been prepared. Metallic organic compounds are represented in the new list by *zinc ethyl* and *tetraphenyl tin*. A new method for the preparation of *anhydrous formic acid* has lowered its price to one-fourth that formerly required.

Altogether more than one hundred fifty substantial downward revisions in price have been made owing to improved methods and lower costs of raw materials. In only a few isolated cases have special conditions made an increase necessary. We are glad to note this continued progress in manufacturing new chemicals and reducing the cost of the ones previously listed, which has resulted in a greater demand for these products, even in a time of diminished business activity.

(Continued from page 2)

also little affected by acetic acid. It is obtained quantitatively from sodium acetate solutions containing as much as 25% acetic acid. Nickel behaves similarly but the optimum concentration of acetic acid is approximately 5 to 10%. Manganese precipitates only in neutral or faintly acid solutions so it can easily be separated from iron by first removing the iron in a more strongly acid medium. In this respect, manganese behaves very much like magnesium and can, therefore, be separated from zinc in the manner previously described for magnesium. The iron precipitate is obtained free of aluminum by first adding enough malonic or tartaric acid to form a complex aluminum salt which stays in solution.

At the present time 8-hydroxyquinoline is used principally on account of its excellence as an aluminum precipitant. The method for magnesium seems to be growing in favor, however, and it is quite possible that the solubility differences of some of the other metallic hydroxyquinoline compounds will result in a much wider use of this reagent in quantitative analysis.

Eastman Organic Chemicals as Analytical Reagents

XVIII. REAGENTS FOR COPPER

SODIUM DIETHYLDITHIOCARBAMATE

Callan and Henderson: *Analyst* 54, 650 (1929)

The solution containing copper, freed from other metals when necessary, is made up to a suitable volume in a measuring flask and an aliquot portion pipetted into a 100 cc. Nessler cylinder. It is then diluted with water, and made slightly ammoniacal (or strongly ammoniacal if zinc is present). Ten cubic centimeters of a 0.1% aqueous solution of the reagent and sufficient water to bring the volume to the 100 cc. mark are added. After mixing well, the yellow color is compared with that of similar tubes

containing known quantities of copper. The amount of copper in the solution to be tested should not exceed 0.0001 gm. per 100 cc. as above this concentration the depth of color becomes too great for satisfactory matching.

P-DIMETHYLAMINO BENZAL-RHODANINE
Kolthoff: *J. A. C. S.* 52, 2222 (1930)

This reagent, recommended originally by Feigl, is used in the form of its saturated alcoholic solution. Since it is most sensitive to copper in the cuprous form, small amounts of hydrazine sulfate are added to the copper solution under examination. The solution is then treated with a slight excess of 6N ammonia and about 0.2 cc. of the organic reagent. A brown to violet color is obtained, depending on the amount of copper present. The maximum intensity of color is gained by allowing the ammoniacal solution to stand for five minutes and then acidifying with 30% acetic acid. A solution containing as little as 0.3 mg. of copper per liter gives a distinct red-brown color.

New Eastman Organic Chemicals

These chemicals were added to our stock too late for classification in List No. 22; specifications and prices will be found on page 9 of the catalog.

- * *p*-Aminodimethylaniline
- Antimony Trifluoride
- * β -Benzoyl Acrylic Acid
- * β -Bromo-*n*-propyl Acetate
- * β -Diethylaminopropyl Alcohol
- * Disodium *m*-Sulfobenzoate
- * Ethyl *S*-Methylxanthate
- * Ethyl Nitrite
- * Ethyl Nitrite (50% in isopropyl alcohol)
- * Methyl *p*-Hydroxybenzoate
- * β -Phenylpropionamide
- * Pyrogallol Triacetate
- * Thiophenylacetamide
- * *Manufactured or purified in our Kodak Park laboratories.*